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Kinetic Modeling of Isothermal or Non-isothermal Adsorption in a Pellet: Application to Adsorption Heat Pumps

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Abstract   Understanding the interaction between a fluid and a solid phase is of fundamental importance to the design of an adsorption process. Because the heat effects associated with adsorption are comparatively large, the assumption of isothermal behavior is a valid approximation only when uptake rates are relatively slow. In this article, we propose to determine when it is needed to choose the isothermal or non-isothermal assumption according to two physical parameters α (ratio convection/capacity) and β (quantity of energy/capacity). The proposed problem is solved by a mathematical method in the Laplace domain. When $\alpha \to \infty$ (infinitely high heat transfer coefficient) or $\beta \to 0$ (infinitely large heat capacity), the limiting case is isothermal. When the diffusion is rapid ($\alpha < 10$) the kinetics of sorption is controlled entirely by heat transfer. If the adsorption process is to be used as a heat pump, it shall be represented by an isotherm model with α and β as high as possible.
Keywords   adsorption, non-isothermal, energy, pellet

1   INTRODUCTION

Since the early 1960s, separation processes by adsorption, such as pressure swing adsorption or thermal swing adsorption, have become important industrial operations [1, 2]. At present, an application in the field of adsorption heat pumps (AHPs) represents one of the most promising technical applications of the adsorption process. Understanding the interaction between a fluid and a solid phase is of fundamental importance to the design of an adsorption process. These cyclic processes are based on a parallel arrangement of columns packed with adsorbent pellets. Because the heat effects associated with adsorption are comparatively great, the assumption of isothermal behavior is a valid approximation only when uptake rates are relatively slow.

A basic adsorption heat pump cycle consists of four main parts: an adsorber, which is a container filled with an adsorbent (such as zeolite, active carbon, silica gel), a condenser, an evaporator, and an expansion valve. Basically, an adsorption heat pump operates by cycling adsorbate between adsorber, condenser, and evaporator. In the adsorption heat pump cycle, adsorption phenomena play the same role of mechanical power, so that the working fluid can be circulated in the cycle without any mechanical power [3]. An adsorption heat pump cycle consists of four steps, which are isosteric heating (*a–b*), isobaric desorption (*b–c*), isosteric cooling (*c–d*) and isobaric adsorption (*d–a*) as shown in Fig. 1.

In recent years, the importance of adsorption heat pumps and adsorption refrigeration systems has increased since these systems can directly utilize the
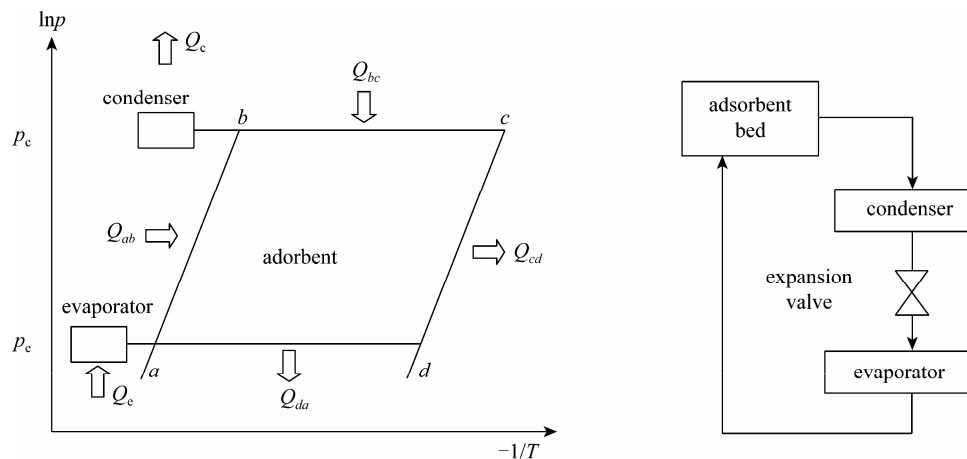

Figure 1   Thermodynamic cycle of a basic adsorption heat pump

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primary thermal energy sources and additionally the waste heat generated in various industrial processes. The important advantages of the adsorption heat pumps can be described as follows [3]:

• they can operate with thermal driving energy sources such as waste heat, solar, and geothermal energies;

• they can work with low temperature driving energy sources;

• they do not require moving parts for circulation of working fluid;

• they have long life time;

• they operate without noise and vibration;

• they have simple principle of working;

• they do not require frequent maintenance;

• they are environmental friendly since they do not contain any hazardous materials for environment; and

• they can be employed as thermal energy storage device.

On the contrary, the main disadvantages of the adsorption heat pump systems are as follows:

• they have low COP values;

• they are intermittently working principles;

• they require high technology and special design to maintain high vacuum with working pairs used such as zeolite-water, silica gel-water, and activated carbon-methanol;

• they have large volume and mass relative to traditional mechanical heat pump systems.

AHPs are thermally driven and can, therefore, make use of waste heat as well as thermal renewable energy resources. Moreover, AHPs can utilize high energy fuels more effectively than modern condensing boiler heating systems and, consequently, a reasonable amount of the resulting environmental pollution could be avoided. One of the most interesting working pairs for AHPs is zeolite-water, which is non-poisonous, non-flammable and, moreover, has no ozone depletion potential. The adsorption of water vapor into a porous solid adsorbent, such as zeolite, results in the release of the heat of adsorption. Accordingly, the temperature of the adsorbent particle rises, which reduces its water uptake capacity. Therefore, the heat of adsorption has to be removed before further mass transfer of vapor into the adsorbent particle takes place. The evaluation of the heat and mass transfer rates accompanying such an adsorption process is therefore a very important aspect in designing and optimizing the operation of an adsorption heat pump.

Many experimental studies were realized during the last twenty years to analyze the influence of various parameters in transient period [4–6]. Bonnissel *et al*. [7] studied a rapid thermal swing adsorption process based on a composite adsorbent bed. The high effective conductivity of the bed and the fast dynamics of the thermoelectric elements allow the cycles (cooling and adsorption/heating and desorption) to be run in 10–20 min. A model based on experimental results is developed that accounts for the usual mechanisms of equilibrium and heat- and mass-transfer kinetics in adsorption, coupled with the specific dynamic behavior of the thermoelectric elements.

Moreover, many studied were realized in the thermal effects in a spherical adsorbent pellet [8–15]. For each model, some hypotheses were assumed.

During adsorption, the heat generated is partly transferred to the surrounding fluid and is partly accumulated in the particle, leading to a temperature increase. The calculation of the temperature uptake curves is based on mathematical models of different complexity depending on the simplifying assumptions being made. The most widely applied simplifying assumptions are as follows [14].

(1) The isotherm is linear. This assumption is particularly useful in the derivation of analytical solutions of the model equations [8]. In most practical systems, however, the isotherms are nonlinear and then these models are inaccurate. The linearization of the isotherm leads to the underestimation of the intraparticle mass-transfer rate and consequently the predicted maximum particle temperature is lower than that observed.

(2) The external mass-transfer resistances are negligible. This assumption is rather controversial because at the initial stages of the process when the heat effects are most significant, the external mass-transfer resistances are usually rate controlling. As shown by Hills [12], this assumption leads to greater errors than the assumption that the isotherm is temperature independent.

(3) The adsorption isotherm parameters are independent of temperature. As shown by Hills [12], in the case of small temperature rises (less than 10 K), the assumption does not lead to significant errors.

(4) The diffusion coefficient, heat capacity and heat of sorption are independent of temperature.

(5) The particle temperature gradients are negligible and the heat transfer resistance is contributed by the film surrounding the particle. As shown by Brunovska *et al*. [16] the lumped thermal model of nonisothermal adsorption is a very good approximation to the complete model for many practical systems.

(6) The intraparticle mass-transfer rate can be approximated using driving force models. Bowen and Rimmer [17] applied Vermeulen's quadratic driving force model [18] in the analysis of experimental results for the system of water vapor-alumina. Bhaskar and Do [19] developed approximate models for nonisothermal adsorption with a linear isotherm using the parabolic (LDF model) and the *n*th order approximation of the intraparticle concentration profile

In this study, a methodology to choose a good adsorbent in particular according to its thermodynamic properties is presented. We focus our attention on the interaction fluid/solid. The simplest case to consider is a single microporous adsorbent particle exposed to a step change in sorbate concentration at the external surface of the particle at time zero. Heat transfer is assumed to be sufficiently rapid relative to the sorption rate, so that temperature gradients both through the particle and between particle and surrounding fluid are negligible. Two cases are considered, isothermal condition and adsorption behavior with temperature effect. A mathematical development is presented for

each case. According to two developed parameters α (ratio convection/capacity) and β (quantity of energy/capacity), the difference between isothermal and non-isothermal is analyzed.

2 ISOTHERMAL ASSUMPTIONS

During adsorption, heat is generated, which is partly transferred to the surrounding fluid and partly accumulated in the particle leading to an increase of temperature. The calculation of the temperature uptake curves is based on mathematical model of different complexity depending on the simplifying assumptions being made. Since adsorption is exothermic and the heat of sorption must be dissipated by the heat transfer, there is, in general, a difference in temperature between the adsorbent particle and the ambient fluid when sorption is taking place. Whether or not this temperature difference is significant depends on the relative rates of mass and heat transfer. By the simple theoretical analysis it may be shown that in a batch adsorption experiment it is the dissipation of heat from the external surface of the adsorbent sample, rather than the conduction of heat within the adsorbent, that is generally the rate limiting heat transfer process. When the heat transfer resistance may be neglected, the system is treated as isothermal case.

First, we consider some isothermal conditions in the pellet and the isotherm is $q = q_0$. The isotherm is supposed to relate the concentration q inside the pellet (or at the external boundary) to the concentration of the external fluid. Another basic assumption is that the pellet is treated as a homogenous medium (contact with the fluid occurs only at the external boundary). Thus, the diffusivity D_c is constant in the pellet.

The system is modeled by the following equations:

$$
\begin{cases}
\dfrac{\partial q}{\partial t} = D_c \left(\dfrac{\partial^2 q}{\partial r^2} + \dfrac{2}{r} \dfrac{\partial q}{\partial r} \right) & \forall t > 0, \forall r(0^+ < r < r_c) \\[2mm]
q(r, t = 0) = q_0' & \forall r(0^+ < r < r_c) \\[2mm]
q(r_c, t) = q_0 & \forall t > 0 \\[2mm]
\left. \dfrac{\partial q}{\partial r} \right|_{r=0^+} = 0 & \forall t > 0
\end{cases} \tag{1}
$$

Using the method based on a separation of variables with $q(r, t) = T(t)R(r)$, and using superposition of the elementary solutions, we obtain

$$
q = q_0 + 2\left(q_0' - q_0 \right) \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{\lambda_n r} \sin\left(\lambda_n r \right) e^{-\lambda_n^2 D_c t} \tag{2}
$$

If $u = (q - q_0)/(q_0' - q_0)$ represents the reduced concentration in the pellet, $\eta = r/r_c$ the reduced radius and $\tau = D_c t / r_c^2$ the reduced time,

$$
u(\eta, \tau) = 2 \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n\pi\eta} \sin\left(n\pi\eta \right) e^{-n^2\pi^2\tau} \tag{3}
$$

Figure 2 represents the 3D evolution of u *versus* the radius and reduced time (step in time 0.01; step in radius 0.05).
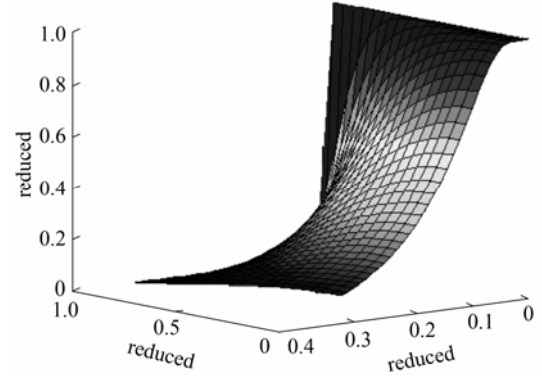

Figure 2   3D representation of reduced concentration according to radius and time

The value $q(r_c, t)$ is equal to $q_0 \neq 0$, for solving the system analytically.

With $\tau = D_c t / r_c$, the analytic solution is given by the familiar expression

$$
\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2\pi^2\tau}}{n^2} \tag{4}
$$

where m_t represents the quantity adsorbed in the pellet at time t and m_∞ the quantity adsorbed in the pellet at final time. We denote $\overline{Q}(\tau) = m_t / m_\infty$.

In practice m_t / m_∞ will be approximated by [8]

$$
\overline{Q}_N(\tau) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{N} \frac{e^{-n^2\pi^2\tau}}{n^2} \tag{5}
$$

Figure 3 shows different approximations and it seems that the convergence is quite fast. Starting from $N = 5$, we cannot see any difference in $\overline{Q}_N(\tau)$ from the graph. Let us check it by the following simple error estimation:
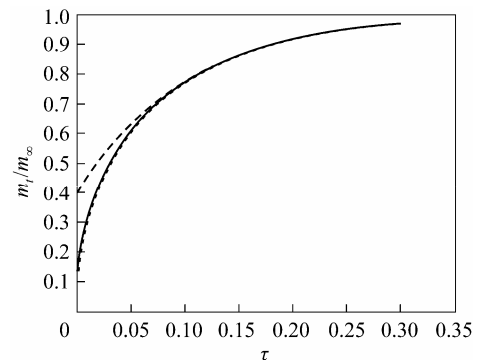

Figure 3   Numerical approximation on m_t/m_∞ values *versus* the reduced time τ
---- $n = 1$; —— $n = 5$; ····· $n = 10$

$$\left|\bar{Q}(\tau) - \bar{Q}_N(\tau)\right| = \frac{6}{\pi^2} \sum_{n=N+1}^{\infty} \frac{e^{-n^2\pi^2\tau}}{n^2}$$

$$\leqslant \frac{6}{\pi^2} \sum_{n=N+1}^{\infty} \frac{1}{n^2} \leqslant \frac{6}{\pi^2} \int_N^{\infty} \frac{dx}{x^2} = \frac{6}{\pi^2 N} \quad (6)$$

This gives an approximate absolute error of 0.12 for $N = 5$. In reality, the error is much smaller if τ stays away from zero. Indeed, if $\tau \geqslant \tau_0 \geqslant 0$, the upper estimation can be improved to the following exponential error bound

$$\left|\bar{Q}(\tau) - \bar{Q}_N(t)\right| = \frac{6}{\pi^2} \int_N^{\infty} \frac{e^{-n^2\pi^2\tau_0}}{x^2} dx \leqslant \frac{3}{\pi^4\tau_0} \frac{e^{-N^2\pi^2\tau_0}}{N^3} \quad (7)$$

For example, if the reduced time is at least $\tau_0 = 0.01$ and $N = 5$, we get for the absolute error a much better approximation of 0.000418.

3 NON-ISOTHERMAL ASSUMPTIONS

In this case, we assume that intracrystalline diffusion is the only significant resistance to the mass transfer. The sorbate concentration at the surface of each particle in the sample is therefore always in equilibrium, at the temperature of the sample, with the sorbate concentration in the ambient fluid. In addition, the thermal conductivity is assumed to maintain an essentially uniform temperature throughout the entire adsorbent particle. The rate of heat transfer between the adsorbent and the ambient fluid, which is assumed to obey Newton's law, is finite, so that during the transient adsorption there is a time-dependent temperature difference between the adsorbent and ambient fluid. The system is subjected, at time zero, to a small difference step change in ambient sorbate concentration from a previously established equilibrium condition. We assume that the concentration equilibrium between fluid phase and adsorbed phase is established quickly at the free surface of the pellet and the equilibrium adsorbed phase concentration is assumed to vary linearly with both temperature and fluid phase concentration. Subject to these approximations, the system may be described by the following equation in reduced values $Q = q(t)/q_\infty$, $\eta = r/r_c$ and $\tau = D_c t/r_c^2$.

In opposite to the previous part, the reduced values permit to find an analytic solution in the Laplace domain. The mathematical model is

$$\frac{\partial Q}{\partial \tau} = \frac{1}{\eta^2} \frac{\partial}{\partial \eta}\left(\eta^2 \frac{\partial Q}{\partial \tau}\right) \quad (8a)$$

$$Q(\eta, \tau) = 0, (\tau < 0) \qquad Q(\eta, 0^+) = 0, \text{ (if } 0 \leqslant \eta < 1) \quad (8b)$$

$$Q(1, \tau) = Q_s(T) \quad (8c)$$

$$\left.\frac{\partial Q}{\partial \eta}\right|_{\eta=0} = 0 \quad (8d)$$

$$\rho(-\Delta H)\frac{d\bar{Q}}{d\tau} = \frac{\rho c_p}{q_\infty - q_0}\frac{dT}{d\tau} + \frac{ha}{q_\infty - q_0}\frac{(T - T_0)}{D/r_c} \quad (8e)$$

The equilibrium relationship at the crystal surface is assumed to be linear with respect to both concentration and temperature:

$$Q_s = 1 + \frac{\partial q^*}{\partial T}\left(\frac{T - T_0}{q_\infty - q_0}\right) \quad (8f)$$

Equation (8a) is written in the Laplace domain, and $\tilde{Q}(\eta, p)$ is a root of

$$p\tilde{Q} - Q(\eta, 0) = \frac{1}{\eta^2}\frac{\partial}{\partial \eta}\left(\eta^2 \frac{\partial \tilde{Q}}{\partial \eta}\right) = \frac{\partial^2 \tilde{Q}}{\partial \eta^2} + \frac{2}{\eta}\frac{\partial \tilde{Q}}{\partial \eta} = p\tilde{Q}$$

$$\text{because} \quad Q(\eta, 0^+) = 0 \quad (9)$$

The determination of $\tilde{Q}(\eta, p)$ is presented in Appendix A, in which we obtain

$$\forall p : \tilde{Q}(\eta, p) = a_0 \frac{\text{sh}\left(\eta\sqrt{p}\right)}{\eta\sqrt{p}}; \quad a_0 \in \Re \quad (10)$$

Thus,

$$\forall p : \tilde{Q}(\eta, p) = \tilde{Q}_s(p)\frac{\text{sh}\left(\eta\sqrt{p}\right)}{\eta\text{sh}\left(\sqrt{p}\right)} \quad (11)$$

In the Laplace domain, $\tilde{\bar{Q}}(p)$ represents the average concentration $\bar{Q}$ in the pellet

$$\tilde{\bar{Q}}(p) = 3\int_0^1 \tilde{Q}(\eta, p)\eta^2 d\eta = 3\frac{\tilde{Q}_s(p)}{\text{sh}\left(\sqrt{p}\right)}\int_0^1 \frac{\text{sh}\left(\eta\sqrt{p}\right)}{\eta}\eta^2 d\eta$$

$$(12)$$

$$\text{so} \quad \tilde{\bar{Q}}(p) = 3\frac{\tilde{Q}_s(p)}{p}\left[\sqrt{p}\coth\left(\sqrt{p}\right) - 1\right] \quad (13)$$

With Eqs. (8e) and (8f), we have the following equation

$$\rho(-\Delta H)\frac{d\bar{Q}}{d\tau} = \frac{\rho c_p}{q_\infty - q_0}\frac{dT}{d\tau} + \frac{ha}{D/r_c}\frac{(Q_s - 1)}{\left(\frac{\partial q^*}{\partial T}\right)} \quad (14)$$

With Eq. (8f), $\dfrac{dT}{d\tau} = \dfrac{dQ_s}{d\tau}\dfrac{(q_\infty - q_0)}{\left(\dfrac{\partial q^*}{\partial T}\right)}$, Eq. (14) becomes

$$(-\Delta H)\frac{\left(\frac{\partial q^*}{\partial T}\right)}{c_p}\frac{d\bar{Q}}{d\tau} = \frac{dQ_s}{d\tau} + \frac{ha}{D/r_c}\frac{(Q_s - 1)}{\rho c_p} \quad (15)$$

With $\alpha = \dfrac{ha}{\rho c_p}\dfrac{r_c}{D}$ and $\beta = \dfrac{\Delta H}{c_p}\left(\dfrac{\partial q^*}{\partial T}\right)$, Eq. (15) becomes

$$\beta \frac{d\overline{Q}}{d\tau} + \frac{dQ_s}{d\tau} = \alpha(1 - Q_s) \qquad (16)$$

In the Laplace domain, Eq. (16) is

$$\beta p \tilde{\overline{Q}}(p) + (\alpha + p)\tilde{Q}_s(p) = \frac{\alpha}{p} + 1 \qquad (17)$$

Equations (13) and (17) allow us to write

$$\tilde{Q}_s(p) = \frac{(\alpha + p)}{p\left\{3\beta\left[\sqrt{p} \cdot \coth\left(\sqrt{p}\right) - 1\right] + (\alpha + p)\right\}} \qquad (18)$$

Finally, transferring $\tilde{Q}_s(p)$ in Eq. (17), we obtain

$$\tilde{\overline{Q}}(p) = \frac{3(\alpha + p)\left[\sqrt{p} \cdot \coth\left(\sqrt{p}\right) - 1\right]}{p^2\left\{3\beta\left[\sqrt{p} \cdot \coth\left(\sqrt{p}\right) - 1\right] + (\alpha + p)\right\}} \qquad (19)$$

The method to obtain the original $\overline{Q}(\tau)$ from $\tilde{\overline{Q}}(p)$ is presented in Appendix B, which shows
$$\overline{Q}(\tau) = 1 +$$

$$\sum_{n=1}^{\infty} \frac{-9\left[\dfrac{\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1}{p_n}\right]^2 e^{p_n\tau}}{\dfrac{1}{\beta} + \dfrac{3}{2}\left[\sqrt{p_n}\coth\left(\sqrt{p_n}\right) \cdot \dfrac{1 - \sqrt{p_n}\coth\left(\sqrt{p_n}\right)}{p_n} + 1\right]}$$
$$p_n \in C \qquad (20)$$

The restriction in the real domain is presented in Appendix C. The final result is [1]

$$\overline{Q}(\tau) = 1 + \sum_{n=1}^{\infty} \frac{-9\left[\dfrac{q_n\cot\left(q_n\right) - 1}{q_n^2}\right]^2 e^{-q_n^2\tau}}{\dfrac{1}{\beta} + \dfrac{3}{2}\left[q_n\cot\left(q_n\right) \cdot \dfrac{q_n\cot\left(q_n\right) - 1}{q_n^2} + 1\right]}$$
$$q_n \in \Re \qquad (21)$$

where q_n are the roots of the following equation [1]:

$$\left(\alpha - q_n^2 - 3\beta\right)\sin\left(q_n\right) + 3\beta q_n\cos\left(q_n\right) = 0 \qquad (22)$$

The parameters α and β are variables in a first approach used to solve the PDE system. The two parameters represent respectively the ratio of conductivity to heat capacity and the ratio of the quantity of energy and heat capacity.

4 LOCATION OF THE ROOTS q_n AND DISCUSSION OF THE SOLUTION $\overline{Q}$

In order to understand the solution $\overline{Q}$ we first discuss the roots of the transcendental Eq. (17). Then we give an error estimation of the Nth approximation of $\overline{Q}$ similar to the one obtained in the isothermal case.

4.1 Location of the roots

Let us have a look on the particular situation $\beta = 0$, which implies infinitely large heat capacity and corresponds to the isothermal case. Then Eq. (22) becomes simply $\left(\alpha - q_n^2\right)\sin\left(q_n\right) = 0$ and the roots are $q_n = n\pi$, $n \in N$ plus a special root $q' = \sqrt{\alpha}$.

The general case is not so much different. Suppose $\beta > 0$, then it is easy to conclude from the periodicity of the sine and cosine functions that every interval of the form $[n\pi, (m+1)\pi]$ contains exactly one root qn of Eq. (22). In addition, there is one more special root, say q', coming from the factor $\left(\alpha - q_n^2 - 3\beta\right)$ in Eq. (22). The location of q' depends on the sign of $(\alpha - 3\beta)$.

If $\alpha - 3\beta > 0$, then $q' \approx \sqrt{\alpha - 3\beta}$. More precisely, we have that $\left|q' - \sqrt{\alpha - 3\beta}\right| \leqslant \pi$.

If $\alpha - 3\beta \leqslant 0$, then $q' \in (0, \pi/2)$.

In particular, one must take care of this root in the numerical approximations of $\overline{Q}$ if $(\alpha - 3\beta)$ is small or negative.

4.2 Error bound

We first have to find a more convenient expression of $\overline{Q}$ since the one given in Eq. (17) is not suitable. Consider again the case $\beta = 0$. Then $\cot(q_n)$ is not defined since $q_n = n\pi$. In order to do this, let us start with Eq. (26), from which follows that

$$3\beta q_n\cot\left(q_n\right) = q_n^2 - \alpha + 3\beta \quad \text{and}$$

$$q_n\cot\left(q_n\right) - 1 = \frac{q_n^2 - \alpha}{3\beta}$$

We, therefore, can reformulate the coefficients of the series in Eq. (17)

$$c_n = \frac{\left(\dfrac{q_n^2 - \alpha}{q_n^2}\right)^2}{9\beta + \dfrac{3}{2\left[\left(q_n^2 - \alpha + 3\beta\right)\dfrac{\left(q_n^2 - \alpha\right)}{q_n^2} + 9\beta^2\right]}}$$

$$= \frac{\left(q_n^2 - \alpha\right)^2}{3\beta\left[3(1 + \beta)q_n^2 - \alpha\right] + \left(q_n^2 - \alpha\right)^2}\frac{2}{3q_n^2} \qquad (23)$$

which finally leads to the expression

$$\overline{Q}(\tau) = 1 - 6\sum_{n=1}^{\infty} C_n\frac{e^{-q_n^2\tau}}{q_n^2} \quad \text{with}$$

$$C_n = \frac{\left(q_n^2 - \alpha\right)^2}{3\beta\left[3(1+\beta)q_n^2 - \alpha\right] + \left(q_n^2 - \alpha\right)^2} \qquad (24)$$

Notice that, from this expression, one can see very well that this solution converges to the isothermal situation when $\beta \to 0$ (and that the coefficient, say $C' = C'(\beta)$, corresponding to the special roots q' disappears at the limit).

For the numerical approximation of the solution we have again a good estimate for $\left|\bar{Q} - \bar{Q}_N\right|$, where $\bar{Q}_N(\tau) = 1 - 6\sum_{n=1}^{N} C_n\left(\mathrm{e}^{-q_n^2\tau}/q_n^2\right)$. Since we have precise information on the locations of q_n, we can proceed like in the isothermal case. Let us first focus on the sign of $B = 3\beta\left[3(1+\beta)q_n^2 - \alpha\right]$. There are two cases.

Case 1: If $B \geqslant 0$ then we have immediately $C_n \leqslant 1$.

Case 2: $B < 0$. If $-\frac{1}{2}\left(q_n^2 - \alpha\right)^2 \leqslant B < 0$, then, similar to case 1, we get

$$|C_n| \leqslant \frac{\left(q_n^2 - \alpha\right)^2}{\left(q_n^2 - \alpha\right)^2 - \frac{1}{2}\left(q_n^2 - \alpha\right)^2} = 2.$$

The remaining situation $B < -\frac{1}{2}\left(q_n^2 - \alpha\right)^2$ is equivalent to

$$\frac{1}{2}\alpha^2 - \alpha\left(3\beta + q_n^2\right) < -\frac{1}{2}q_n^4 - 9(1+\beta)q_n^2$$

The right hand term of this inequality is negative and the left hand term is strictly positive while $\alpha > 2q_n^2 + 6\beta$. However, since $B < 0$, which implies that $\alpha > 3(1+\beta)q_n^2 = \left(2q_n^2 + 6\beta\right) + q_n^2 + 3\left(q_n^2 - 2\right)$, we see that this last situation never occurs while $q_n > \sqrt{2}$.

Finally we get $|C_n| \leqslant 2$ for every $n \geqslant 2$ and for every α and β.

We can now proceed like in the isothermal case. Let us simply indicate how to get the estimation corresponding to the first differential Eq. (1). In order to do so, we make the convention that the summation of the approximation $\overline{Q_N}$ is taken over the first N roots plus the special one q' if $q' \leqslant N\pi$. If $q' > N\pi$ then we have the following estimation (otherwise the error is a little smaller):

$$\left|\bar{Q}(\tau) - \overline{Q_N}(\tau)\right| \leqslant 12\left(\frac{\mathrm{e}^{-q'^2}}{q'^2} + \sum_{n=N+1}^{\infty}\frac{\mathrm{e}^{-q_n^2\tau}}{q_n^2}\right)$$

$$\leqslant 12\left[\frac{\mathrm{e}^{-(N\pi)^2}}{(N\pi)^2} + \sum_{n=N+1}^{\infty}\frac{\mathrm{e}^{-(n\pi)^2\tau}}{(n\pi)^2}\right]$$

$$\leqslant \frac{12}{\pi^2}\left(\frac{1}{N^2} + \frac{1}{N}\right)$$

for every $N \geqslant 2$ \qquad (25)

which is about two times the error estimation obtained in the isothermal case. If the reduced time $\tau \geqslant \tau_0 > 0$, then one has again the exponential decay of the error like in Eq. (6) due to the factor $\mathrm{e}^{-N^2\pi^2\tau_0}$.

5 DIFFERENCE BETWEEN NON-ISOTHERMAL AND ISOTHERMAL CASES

The adsorption characteristics of water vapor on zeolite are essential data in determining the energetic performance of adsorption chillers. From the viewpoint of the fundamental design of adsorption chillers, the investigation of the adsorption isotherm is pertinent for the purpose of system modeling.

In terms of the adsorption chiller performance, the adsorbent must have good thermal conductivity as well as a large specific surface area. To estimate dynamic adsorption capacity using the parameter, we compare the two assumptions, isothermal or non-isothermal. In Table 1, we summarize the data used [20−23]. In this case, we found $\alpha = 16.3$ and $\beta = 2.07$.

Figure 4 shows the difference between the two models. In the non-isothermal model, the uptake curve commonly shows a rapid initial uptake followed by a slow approach to equilibrium because the external
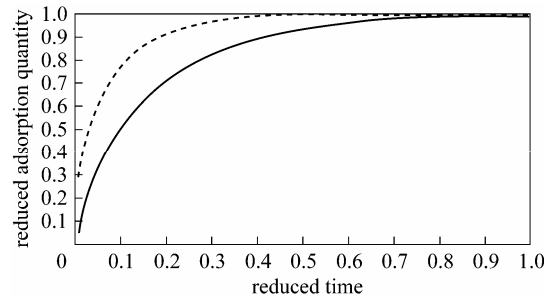

Figure 4 Comparison between isothermal and non-isothermal adsorption kinetics for water on zeolite
—— non isothermal; ---- isothermal

Table 1 The used values found in the literature

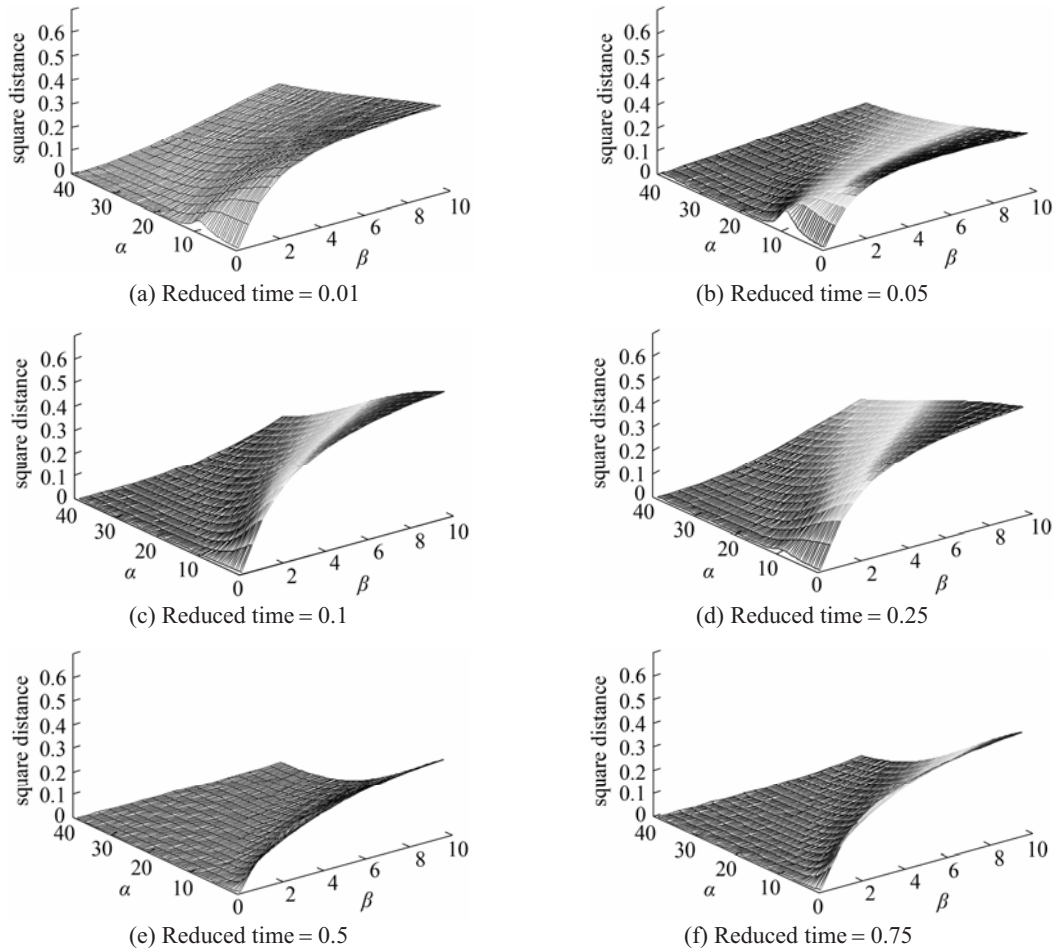| ΔH/kJ·mol^{-1}	$(\partial q^*/\partial T)$/mol·kg^{-1}·K^{-1}	c_p/J·kg^{-1}·K^{-1}	h/m^2·K·W^{-1}	a/m^{-1}	r_c/mm	ρ/kg·m^{-3}	D/m^2·s^{-1}
−36	−0.053	920	10	2.48	1.1	1100	2×10^{-9}

Figure 5   Square distance between the isothermal and non-isothermal model for different α value between 0 to 40 and for different β value between 0 to 10

heat transfer controlled the adsorption. Let us recall that the isothermal model represents the ideal condition in the heat adsorption process.

In the isothermal case, the equilibrium is reached very quickly. The maximum difference between the two models is obtained in the first phase of the batch adsorption. This phenomenon is due to the fast temperature rising when the adsorption starts. The heat of adsorption produced in the pellet is not transferred into the fluid due to the external heat transfer. In Fig. 5, different graphs represent the square distance between the adsorbed quantity with an isothermal model and a non-isothermal assumption at different reduced time. For the calculation, the number of terms N is 20, and the α value is between 0 and 40 and β between 0 and 10. If α is close to zero and β is large, we observe that when the reduced time is lower than 0.25, the calculated errors increases with the reduced time. And when the reduced time is higher than 0.25, the calculated errors decreases.

To increase the process efficiency, it is necessary to raise the external heat transfer. It can be modified by the hydrodynamics around the pellet. The values of α and β can determine the "efficiency" of the heat adsorption process. If the β value is small and/or close to

zero, the adsorption curve can be analyzed as in the isothermal case. However, this means that the heat pump process cannot be operated because it will not produce enough heat. The α value is more significant, because it represents the ratio of the convection to the thermal capacity. To reach the ideal case, α should be very large. The external heat transfer will then not be a limiting phenomenon, and the adsorption is close to the isothermal case.

6   CONCLUSIONS

In this article, we show the importance of the pellet adsorption study before designing a heat adsorption process. The difference between the two models, isothermal or non-isothermal, could be measured by the values of two parameters α and β. When $\alpha \rightarrow \infty$ (infinitely high heat transfer coefficient) or $\beta \rightarrow 0$ (infinitely large heat capacity), the limiting case is isothermal. When the diffusion is rapid (small α) the kinetics of sorption is controlled entirely by heat transfer. If the adsorption process is to be used as a heat pump, it shall be represented by an isotherm model with α and β as high as possible. Then, these

two parameters could determine if the couple adsorbent/ adsorbate can be used in the case of an adsorption heat pump process.

NOMENCLATURE

a	external surface area per unit particle volume
c_p	heat capacity
D	diffusivity
h	heat transfer coefficient
ΔH	adsorption enthalpy
m_t	mass adsorbed per unit of adsorbent during time $t (= q - q_0')$
m_∞	mass adsorbed per unit of adsorbent during the equilibrium time $(= q_\infty - q_0')$
Q	reduced mass adsorbed $(= q / q_\infty)$
Q_s	reduced mass adsorbed for $r = r_c$
$\bar{Q}$	reduced average mass adsorbed
q	mass adsorbed per unit of adsorbent
q_∞	mass adsorbed per unit of adsorbent at equilibrium time
q_0	initial mass adsorbed per unit of adsorbent at $r = r_c$
q_0'	initial mass adsorbed per unit of adsorbent
$\bar{q}$	average mass adsorbed per unit of adsorbent
r	radius coordinate of pellet
r_c	pellet radius
t	time
u	reduced concentration in the pellet $[= (q - q_0)/(q_0' - q_0)]$
α	parameter $[= h a r_c /(\rho c_p D)]$
β	parameter $[= \Delta H (\partial q^* / \partial T)/c_p]$
η	reduced radius coordinate
ρ	density, kg·m^{-3}
τ	reduced time $(= D_c t / r_c^2)$

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APPENDIX A Determination of $\tilde{Q}(\eta, p)$

First, we search a solution like an integer serial function using $\tilde{Q}(\eta, p) = \sum a_k \eta^k$. We obtain

$$\sum_{k=1}^{\infty} k(k+1) a_{k+1} \eta^k + 2\sum_{k=0}^{\infty}(k+1)a_{k+1}\eta^k + \sum_{k=1}^{\infty} -p a_{k-1}\eta^k = 0 \quad (A1)$$

And then, we transform the following system

$$\left. \begin{array}{c} k = 0, \ 2a_1 = 0 \\ k \geqslant 1, \ k(k+1)a_{k+1} + 2(k+1)a_{k+1} - p a_{k-1} = 0 \\ \Rightarrow (k+1)(k+2)a_{k+1} - p a_{k-1} = 0 \end{array} \right\} \quad (A2)$$

From $\forall k - 1$ odd, $a_k = 0$ and $\forall k - 1 = 2l$ the recursive formula leads to

$$a_2 = \frac{p a_0}{2 \times 3}, \ a_4 = \frac{p a_2}{4 \times 5} = \frac{p^2 a_0}{2 \times 3 \times 4 \times 5} = \frac{p^2 a_0}{5!}$$

$$\text{so} \quad a_{2l} = \frac{p^l}{(2l+1)!} a_0 \quad (A3)$$

Finally $\tilde{Q}(\eta, p) = a_0 \sum_{l=0}^{\infty} \frac{(p)^l}{(2l+1)!}\eta^{2l}$, so that we can write

$$\tilde{Q}(\eta, p) = \frac{a_0}{\eta \sqrt{p}} \sum_{l=0}^{\infty} \frac{\left(\sqrt{p}\right)^{2(l+1)}}{(2l+1)!}\eta^{2(l+1)} \quad (A4)$$

Thus,

$$\forall p : \tilde{Q}(\eta, p) = a_0 \frac{\text{sh}\left(\eta \sqrt{p}\right)}{\eta \sqrt{p}}; \quad a_0 \in \mathfrak{R} \quad (A5)$$

APPENDIX B Determination of $\tilde{Q}(\tau)$ original of $\tilde{\bar{Q}}(p)$ in the Laplace domain with $p \in C$

To obtain $\bar{Q}(\tau)$ original of $\tilde{\bar{Q}}(p)$, it is necessary to use the residue theorem with just the simple pole-zero.

1. Beginning behavior

We use the development of $\coth\left(\sqrt{p}\right)$ in the vicinity of zero, $\coth\left(\sqrt{p}\right) = \frac{1}{\sqrt{p}}\left[1 + \frac{1}{3}p + O\left(p^2\right)\right]$. It results in $\sqrt{p}\coth\left(\sqrt{p}\right) - 1 = \frac{1}{3}p + O\left(p^2\right)$.

While deferring in Eq. (19), it comes

$$\tilde{\bar{Q}}(p) = \frac{3(\alpha + p)\left[\frac{1}{3}p + O(p^2)\right]}{p^2\left\{3\beta\left[\frac{1}{3}p + O\left(p^2\right)\right] + (\alpha + p)\right\}}$$

$$= \frac{1}{p}\frac{(\alpha + p)\left[1 + O\left(p^2\right)\right]}{(\alpha + p) + \beta p + O\left(p^2\right)} \quad\quad \text{(B1)}$$

$\tilde{\bar{Q}}(p)$ has a simple pole and the residue $\text{Res}\left(\tilde{\bar{Q}}, 0\right) = 1$.

2. Calculation of the residues for the solutions p_n from the equation $g(p) = 3\beta\left[\sqrt{p}\coth\left(\sqrt{p}\right) - 1\right] + \alpha + p = 0$

In the case of a simple pole $\Rightarrow g(p) = (p - p_n)h(p)$

$g'(p) = h(p) + (p - p_n)h'(p)$, from which $g'(p_n) = h(p_n)$ because $g(p_n) = 0$

$$g(p_n) = 0, \quad \coth\left(\sqrt{p_n}\right) = \frac{-p_n - \alpha - 3\beta}{3\beta\sqrt{p_n}} \quad\quad \text{(B2)}$$

$$g'(p) = 3\beta\left[\frac{\coth\left(\sqrt{p}\right)}{2\sqrt{p}} + \frac{1 - \coth^2\left(\sqrt{p}\right)}{2}\right] + 1 \quad\quad \text{(B3)}$$

Thus,

$$\text{Res}\left[\tilde{\bar{Q}}(p)e^{p\tau}, p_n\right] =$$

$$\frac{3(\alpha + p_n)\left[\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1\right]e^{p_n\tau}}{p_n^2\frac{3\beta}{2\sqrt{p_n}}\left\{\coth\left(\sqrt{p_n}\right) + \sqrt{p_n}\left[1 - \coth^2\left(\sqrt{p_n}\right)\right] + \frac{2\sqrt{p_n}}{3\beta}\right\}}$$

(B4)

According to Eq. (B2) $\alpha + p_n = -3\beta\left[\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1\right]$. Therefore,

$$\text{Res}\left[\tilde{\bar{Q}}(p)e^{p\tau}, p_n\right] =$$

$$\frac{3\left\{-3\beta\left[\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1\right]\right\}\left[\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1\right]e^{p_n\tau}}{p_n^2\frac{3\beta}{2\sqrt{p_n}}\left\{\coth\left(\sqrt{p_n}\right) + \sqrt{p_n}\left[1 - \coth^2\left(\sqrt{p_n}\right)\right] + \frac{2\sqrt{p_n}}{3\beta}\right\}}$$

(B5)

$$\text{Res}\left[\tilde{\bar{Q}}(p)e^{p\tau}, p_n\right] =$$

$$\frac{-6\left[\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1\right]^2 e^{p_n\tau}}{\frac{p_n^2}{\sqrt{p_n}}\left\{\coth\left(\sqrt{p_n}\right) + \sqrt{p_n}\left[1 - \coth^2\left(\sqrt{p_n}\right)\right] + \frac{2\sqrt{p_n}}{3\beta}\right\}}$$

(B6)

$$\text{Res}\left[\tilde{\bar{Q}}(p)e^{p\tau}, p_n\right] =$$

$$\frac{-9\left(\frac{\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1}{p_n}\right)^2 e^{p_n\tau}}{\frac{3}{2\sqrt{p_n}}\left\{\coth\left(\sqrt{p_n}\right) + \sqrt{p_n}\left[1 - \coth^2\left(\sqrt{p_n}\right)\right] + \frac{2\sqrt{p_n}}{3\beta}\right\}}$$

(B7)

$$\text{Res}\left[\tilde{\bar{Q}}(p)e^{p\tau}, p_n\right] =$$

$$\frac{-9\left(\frac{\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1}{p_n}\right)^2 e^{p_n\tau}}{\frac{3}{2}\left\{\frac{\coth\left(\sqrt{p_n}\right) + \sqrt{p_n}\left[1 - \coth^2\left(\sqrt{p_n}\right)\right]}{\sqrt{p_n}}\right\} + \frac{1}{\beta}}$$

(B8)

$$\text{Res}\left[\tilde{\bar{Q}}(p)e^{p\tau}, p_n\right] =$$

$$\frac{-9\left(\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1\right)^2 e^{p_n\tau}}{\frac{3}{2}\left\{\frac{\sqrt{p_n}\coth\left(\sqrt{p_n}\right)\left[1 - \sqrt{p_n}\coth\left(\sqrt{p_n}\right)\right]}{p_n} + 1\right\} + \frac{1}{\beta}}$$

(B9)

When we sum the terms, we obtain

$$\bar{Q}(\tau) = 1 + \sum_{n=1}^{\infty}\frac{-9\left(\frac{\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1}{p_n}\right)e^{p_n\tau}}{\frac{1}{\beta} + \frac{3}{2}\left[\sqrt{p_n}\coth\left(\sqrt{p_n}\right)\frac{1 - \sqrt{p_n}\coth\left(\sqrt{p_n}\right)}{p_n} + 1\right]}$$

(B10)

where p_n are the roots of the following equation

$$3\beta\left[\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1\right] + \alpha + p_n = 0 \quad\quad \text{(B11)}$$

APPENDIX C Restriction to the real domain

From Eq. (20) or (B10), the restriction on the real domain is carried out as follows.

By considering Eq. (B11), for a particular value p_n

$$g(p_n) = 3\beta\left[\sqrt{p_n}\coth\left(\sqrt{p_n}\right) - 1\right] + \alpha + p_n = 0 \quad\quad \text{(C1)}$$

where

$$g(p_n) = 3\beta\left[\sqrt{p_n}\text{ch}\left(\sqrt{p_n}\right) - \text{sh}\left(\sqrt{p_n}\right)\right] + (\alpha + p_n)\text{sh}\left(\sqrt{p_n}\right) = 0$$

(C2)

If $\sqrt{p_n} = iq_n$ where $q_n \in \Re$ from which Eq. (C1) is written, while noting $\varphi(iq_n) = g(p_n)$

$$\varphi(iq_n) = 3\beta\left[iq_n\text{ch}(iq_n) - \text{sh}(iq_n)\right] + \left[\alpha + (iq_n)^2\right]\text{sh}(iq_n) = O$$

(C3)

$$\varphi(iq_n) = \left(\alpha - q_n^2\right)\left(e^{iq_n} - e^{-iq_n}\right) +$$

$$3\beta\left[iq_n\left(e^{iq_n} + e^{-iq_n}\right) - \left(e^{iq_n} - e^{-iq_n}\right)\right] = 0 \quad\quad \text{(C4)}$$

$$\varphi(iq_n) = \left(\alpha - q_n^2\right)2i \cdot \sin(q_n) +$$

$$3\beta\left[iq_n 2 \cdot \cos(q_n) - 2i \cdot \sin(q_n)\right] = 0 \quad\quad \text{(C5)}$$

$$\varphi(iq_n) = 2i\left\{(\alpha - q_n^2)\sin(q_n) + 3\beta[q_n\cos(q_n) - \sin(q_n)]\right\} = 0$$

(C6)

Let us assume that $\psi(q_n) = \dfrac{\varphi(iq_n)}{2i} \in \Re$, it comes

$$\varphi(q_n) = (\alpha - q_n^2 - 3\beta)\sin(q_n) + 3\beta q_n\cos(q_n) = 0 \quad \text{(C7)}$$

According to Eq. (C1),

$$\sqrt{p_n}\coth\left(\sqrt{p_n}\right) = \frac{-\alpha - p_n}{3\beta} + 1 = \frac{q_n^2 - \alpha}{3\beta} + 1 \text{ because}$$

$$p_n = -q_n^2 \quad \text{(C8)}$$

From Eq. (B7)

$$q_n\cot(q_n) = \frac{-\alpha + q_n^2}{3\beta} + 1 = \frac{-\alpha - p_n^2}{3\beta} + 1 \quad \text{(C9)}$$

Thus $\sqrt{p_n}\coth\left(\sqrt{p_n}\right) = q_n\cot(q_n)$. While replacing $\sqrt{p_n}\coth\left(\sqrt{p_n}\right)$ by $q_n\cot(q_n)$ where $q_n \in \Re$, we obtain the following result

$$\bar{Q}(\tau) = 1 + \sum_{n=1}^{\infty} \frac{-9\left(\dfrac{q_n\cot(q_n) - 1}{q_n^2}\right)^2 e^{-q_n^2\tau}}{\dfrac{1}{\beta} + \dfrac{3}{2}\left[q_n\cot(q_n)\dfrac{q_n\cot(q_n) - 1}{q_n^2} + 1\right]} \quad \text{(C10)}$$

Let us recall that q_n are solutions of Eq. (C7), $q_n \in \Re$, which comprises an infinity of solutions.